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(54) Metal fibers obtained by bundled drawing

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Description

The present invention relates to metal fibers obtained by the bundled drawing of wires embedded in a matrix which consists of a different metal than the fibers. After the drawing operation, the matrix material is removed, leaving a bare bundle of fibers. Specifically, the invention also comprises a process and an apparatus for the continuous electrolytic removal of said metal matrix, using the embedded bundle as an anode.

U.S.A. patent 3.379.000 describes the manufacture of stainless steel fibers by bundled drawing, i.e. starting with a bundle of wires embedded in a metal matrix which differs from the wire metal, e.g. in copper sheaths. After the drawing, the copper is stripped in a nitric acid solution. The fibers which are obtained using this patented method still show some traces or remnants of the matrix material (copper) at their surfaces.

To turn the stripping of the matrix metal in HNO_3 into an ecologically sound process, considerable sums must be spent on the neutralizing of the generated nitrogen oxide fumes and on converting the used stripping fluid into disposable waste. Apart from that, some remnants of the metal matrix are left on the fiber surface. Thus, this surface is somewhat contaminated and this can be a disadvantage in certain applications.

With the present invention it is now possible to manufacture metal fibers, using the bundled drawing method as described above and yet avoid this contamination of the fiber surface.

The average concentration of matrix metal in the surface layers of the fibers thus obtained is at the most 0.2 % at. The average copper content in the surface layers of standard metal fibers, obtained by applying the HNO_3 stripping process to a copper matrix, is more than 2 % at. The thickness of the surface layer under consideration is about 50 \AA to 5 nm.

The metal fibers obtained by applying the present invention may be stainless steel fibers with a chromium content of at least 10 % by weight. Specifically, the fibers will contain at least 16 % Cr and also Ni. Furthermore, the invention can be used to manufacture refractory fibers containing Fe, Cr, Al and, optionally, Y or rare earths (as is described, for example, in U.S. patent 4.139.376) and fibers from Ni/Cr alloys, Hastelloy®, Inconel®, titanium or Carpenter®20cb3.

It is also an object of the invention to provide stainless steel fibers of the kind specified above and having a reduced average Chromium content (a lower Cr/Cr + Fe + Ni-ratio) at their surface, i.e. with a Cr/Cr + Fe + Ni-ratio between 1 % and 15 % wherein the Cr, Ni and Fe-contents are expressed in at %. Even if said fibers retain more than 0.2 % at of matrix metal at their surface, the lower Cr-content offers the advantage of a better corrosion resistance as will be explained further on.

The invention also comprehends a process and apparatus for the continuous electrolytic removal of the matrix material from a drawn composite bundle. Thereby, the bundle serves as an anode and the embedded bundle is transported continuously through successive electrolytic baths at a temperature of over 20°C .

A method is known from the published German patent application No. 2.812.576 and from the published British patent application No. 2.032.959 for continuous electrolytic descaling of steel wire by non contact current flow. The steel wire remains entirely submerged in the electrolyte when passing from anode to cathode and thus no transition zones are present interbetween wherein the current is forced to run only through the wire. The Luxembourg patent No. 43.371 deals with the electrolytic removal of a metallic coating from a metallic piece wherein the coated piece is branched as anode.

Contrary to the process and apparatus in such conventional electrolytic stripping installations, transition cells are present between the electrolytic baths. During the process, as defined in claim 1, the bundle is supported at the level or in the vicinity of these transition cells. The arrangement and the distances between the various cells or baths are such that in the spaces between the electrolytic baths and the cathodic transition cells the current is conducted by the bundle. During the process, at least part of the matrix material is deposited on the cathodes facing the bundle in the electrolytic baths. All these measures contribute to the development of a more economical process with the additional advantage of a higher quality fiber product. The fibers are less damaged as will be shown further and some of their characteristics are more constant, i.e. display less variation than in case of standard bundled drawn fibers.

These points will now be explained in more detail on the basis of an embodiment of the invention, illustrating the unexpected additional advantages.

Figure 1 is a diagram of a processing installation for the continuous removal of the matrix material from the bundle.

Figure 2 shows the composition profiles for quantities of Cr and Ni close to the surface of a stainless steel fiber for a bundle obtained by a standard method and for a bundle obtained by applying the present

invention.

For comparison, figure 3 illustrates the variation of the nitrogen content throughout the fiber thickness (close to the surface) of the same two types of fibers.

A series of composite bundles 1, obtained by the usual process of bundled drawing, consisting of several thousands of metal fibers embedded in a body of copper and surrounded by an iron jacket, are transported continuously through an apparatus in accordance with the present invention and specifically through a series of electrolytic baths 2 and 4 for the removal of the metal matrix, i.e. the iron jacket and the body of copper. As schematically represented in figure 1, the iron jacket of bundle 1 is removed by dissolution in a first series of electrolytic baths 2. Subsequently, the bundles 1 pass through a rinsing apparatus 3 and the copper matrix is removed in a next series of electrolytic baths 4. During the process, the copper is recuperated at least in part and preferably in full by deposition on the cathodes 5. This prompt recuperation of metal is an important advantage compared to the earlier treatment with HNO_3 .

In accordance with the invention, cathodic transition cells 6 are placed between the successive baths 2 resp. 4, in which anodes 7 have been mounted - e.g. made of lead - facing the passing bundles 1. On the other hand, in baths 2 resp. 4, the cathode plates 8, resp. 5 have been placed at a distance of several centimeters from the path of the bundle. As a result, current carrying contact elements may be omitted. This was found to be an advantage because, among other things, the current transmission to the bundles by way of mechanical contact (e.g. via rolls) can become increasingly irregular as more matrix material disappears from the bundle.

In general, current transmission by mechanical contact elements causes an additional tensile strain on the bundle as well. As the total processing apparatus can reach a considerable length (especially when aiming for a high and therefore productive processing speed) the bare bundle (as a result of the installation of contact rolls) would have to overcome yet an additional tensile strain at the exit. This would increase the chance of fiber or bundle fracture. The broken off pieces of the fibers might then wind themselves around the contact rolls which could impede the regular transmission of current even more and which could damage the bundle.

In order to minimize current leakage at the transitions between baths and cells, and hence to minimize energy consumption, the overflow sections 9 of successive baths and cells are placed at a sufficient distance from each other so that at least a major part of the electrical current is forced to flow through the bundle in these transition zones 10. Apart from that, this measure promotes the controllability of the electrolytic process.

Preferably, the temperature of the electrolytes in the various baths and cells should be higher than room temperature (over 20°C) ; e.g. $50-60^\circ\text{C}$, in order to increase the efficiency of the matrix removal. In principle, quite some compositions are possible for the electrolytic bath, acidic as well as alkaline. For example, a bath containing sulfuric acid can be used in the section for removing iron (2) as well as in the section for removing copper (4). Obviously, if the metal matrix contains only copper, a copper removal section (9) will suffice. In this case, a suitable electrolyte might contain H_2SO_4 and CuSO_4 . In the baths 2, lead cathodes 8 can be used. However, in the baths 4 it is preferable to use cathodes 5 made of a stronger material (metal) and with less adhesive affinity with respect to the matrix material which has to be deposited. This facilitates the mechanical removal of the layer of metal deposit from these cathodes 5. Naturally, the installation is equipped with pumps 11 and pipes 12 for the circulation of the fluids from the various collectors 14 to the baths 2, 3, 4 and cells 6 and to the respective overflow sections 9. At regular distances in the installation, the bundles are supported by e.g. ceramic cross-bars or combs 13. Preferably, these wear resistant means of support 13 should be mounted at or near the place of the transition zones 10.

It is advisable to use current stabilized rectifiers 15 for the current supply. Current densities between 5 and 75 A per dm^2 of bundle surface were found to be suitable for the iron removal baths. Preferably, the sulfuric acid concentration should be between 200 and 400 g/l. In order to realize an iron removal efficiency of more than 100 % in the baths 2, passivation of the iron jacket must be prevented. This can be achieved by using a relatively low current density (e.g. less than 30 A/dm^2) in the first bath(s). It was also found that this high efficiency can be obtained by limiting the increase of the molar product of the iron ions with the sulfuric acid concentration in the electrolyte. A suitable value for the molar product is, for example, 2.5. The efficiency can become higher than 100 % because, apart from the electrolytic dissolution process of the iron jacket, a simultaneous chemical iron dissolution process occurs as well.

In order to keep the local current density variations within acceptable limits in the electrolytic baths 2 or 4, it turned out to be advisable to select a bath length in the transport direction of the bundle of less than 75 cm. A practically uniform current density distribution in the baths has the advantage of permitting a higher total current without negative effect on the efficiency. Naturally, the cathodic transition cells can be much shorter.

Furthermore, it was found advantageous from the viewpoint of the lowest possible energy consumption and the realization of a uniform current density distribution, to install successive power supply circuits for successive series of baths and to separate these from each other. This separation could be effected, for example, at the level of the cathodic transition cells which are situated between one series of baths and the next. A series of baths may consist of one or more baths. In order to dissolve as little copper as possible in the last electrolytic bath 2, the current here (A/dm^2) will have to remain relatively low. The copper removal baths may have the same composition as the usual copper sulfate/sulfuric acid baths for the electrolytic deposition of copper. Furthermore, the average current densities, normally used in this kind of electrolysis (direct current or pulsating current) were found to be suitable for the invention.

In the discontinuous process for electrolytic removal of the matrix metal from the composite bundle, again the composite acts as an anode. Therefore, the bundle is stored on a metallic supporting frame which is anodically polarized. A convenient frame is e.g. a spool of steel wire equal or similar to that disclosed in U.K. patent No. 1,502,924 onto the core of which the composite bundle is wound in a substantially cylindrical layer. The layer thickness is preferably small in view of permitting a sufficient penetration for the electrolyte which has to dissolve the matrix material during the electrolysis process. The frame with the bundle stored on it is submerged in a bath containing as electrolyte a solution of H_2SO_4 above room temperature. In view of accelerating the dissolution process the electrolyte is either continuously stirred or circulated by means of a pump so as to force on a continuous basis a fresh solution interbetween the neighbouring windings in the cylindrical layer.

Metal plates are suitably arranged in the bath as cathodes thereby facing the outside and/or inside of the cylindrical layer. The plate design and their disposition is of course chosen to avoid a substantial obstruction of the fluid flow through the bath.

The electrical current to the electrodes is supplied by a voltage stabilized rectifier. The voltage is set at a value below 2,5 V. A suitable maximum current is e.g. 20 A per kg of composite to be treated. In this way, the matrix material is completely removed after a run of several hours with an electrolyte at a temperature of almost $50^\circ C$.

Example

A composite bundle of stainless steel fibers with a fiber diameter of $12 \mu m$ of the type AISI-316L, embedded in copper and surrounded by an iron jacket, was treated in the apparatus and according to the continuous process described above. The various values of the current densities, bath lengths, bath concentrations, temperatures etc. were kept within the above mentioned limits.

The resulting fiber bundle, and in particular the composition of its surface layer, was compared to the same bundle 316L which had been stripped in HNO_3 in the standard manner.

The average tensile strength of the fiber obtained by applying the invention was 8.85 % higher than that of the standard stripped fibers, while the variation in the value of the tensile strength over its length was considerably smaller. This is presumably due to the fact that the nitric acid affects the very thin fibers in a more aggressive, irregular and penetrating way than a well regulated electrolytic process.

The results of an analysis of the composition of the surface layer of both types of fibers (Scanning Auger Multiprobe) have been summarized in table 1. The percentages are averages.

Table 1

surface layer ($0.75 \mu m$)	N % at	Cr/Ni %	Cr/Cr + Fe + Ni %	Cu at %
fiber obtained with invention	1	70	7	0
fiber obtained by standard technique	3	220	22	2.3

Figure 2 shows the variation of the Cr/Cr + Fe + Ni-content throughout the fiber thickness for both types of fibers. Curve 17 applies to the fiber bundle which was stripped in HNO_3 while curve 16 applies to the fiber bundle which was treated in accordance with the invention. When HNO_3 is used, the Ni at the fiber surface will be depleted faster than the Cr, while the application of H_2SO_4 has the opposite effect. Therefore, the ratios as shown in figure 2 and table 1 confirm the expected composition changes for both removal processes. It was even established that to strip composite bundles with copper matrixes and fibers from Fe/Cr alloys (possibly with a very low Ni-content) such as AISI-430 types, in HNO_3 is quite difficult. A possible explanation could be the (almost complete) lack of Ni at the fiber surface. However, with th

electrolytic stripping process in $\text{H}_2\text{SO}_4/\text{CuSO}_4$ -baths in accordance with the invention, the copper between these fibers can be removed much faster, probably because of the presence, and thus the depletion possibility, of Cr (16-18 % by weight).

This means that the present invention permits specifically the manufacture of stainless steel fibers made from alloys which contain Ni and at least 16 % Cr by weight whereby the average Cr/Cr + Fe + Ni ratio in the surface layers of these fibers ranges between 1 % and 15 % and wherein the Cr, Ni and Fe contents are expressed in at %. Preferably, this ratio should be less than 10 %. Moreover the average value of the Cr/Ni ratio in the surface layer should be less than 80 %.

The above mentioned average ratio for Cr/Cr + Fe + Ni of less than 10 % as well as said accompanying average ratio for Cr/Ni of less than 80 % is also achievable when the fibers retain more than 0.2 % of matrix material in their surface layer.

In analogy the chromium at the surface of FeCrAl-fibers will be depleted (will decrease) more according to the process of the invention than when stripping the bundle in HNO_3 . This means that the FeCrAl-fibers according to the invention have a lower average Cr-content at their surface than conventional FeCrAl-fibers. Similarly in relatively Ni-rich alloy fibers as Hastelloy®- and Inconel®-fibers stripped according to the invention, the Ni-content at their surface will rise somewhat on the average compared to the same fibers stripped in HNO_3 .

It is immediately apparent from the table that, unlike the fibers which were stripped by a standard method, the fiber which was treated in accordance with the invention, no longer shows any detectable quantities (0 %) of copper at its surface. Furthermore, the nitrogen content in the surface layer of the fiber treated in accordance with the invention, is considerably lower than in case of the standard treatment. Curve 18 in figure 3 shows the variation of the nitrogen content in at % from the fiber surface (0 nm) to a depth of 30 nm for a fiber treated in accordance with the invention. Curve 19 represents the nitrogen variation for the fiber which was treated with HNO_3 . It is remarkable that, as shown in figure 3, the relatively higher nitrogen content in case of standard treatment (curve 19) is also maintained a little further (deeper) below the fiber surface. This could suggest the higher aggressiveness of HNO_3 in comparison to the electrolytic stripping in an H_2SO_4 environment. After all, it was found that the value and variation of the sulfur content at the fiber surface as well as deeper into the fiber was comparable for both types of fibers. If it had been found that a fiber treated in accordance with the invention displayed higher sulphur contents than a fiber treated in the standard way (in HNO_3), we would have to decide on an aggressive attack by H_2SO_4 as well. However, the test results show that this is not the case. Apparently, we can conclude that the electrolytic process in accordance with the invention offers a gentler, less aggressive treatment for very thin fibers.

Therefore, it is a further characteristic of the bundled drawn metal fibers in accordance with the invention, that, on average, they display a lower nitrogen content in their surfaces than the fibers which have been stripped in HNO_3 in the standard way. Therefore, the metal fibers obtained by applying the invention, in particular the stainless steel fibers, will show, on average, a nitrogen content of at most 1.5 at % close to their surfaces.

Finally, both types of fibers were subjected to a corrosion test (Strauss test ASTM standard A 262-86 part E). The weight loss, after remaining 72 hours in a boiling copper sulfate solution, was 23 % for the fiber treated in the standard way and only 15 % for the fiber treated in accordance with the invention. Ergo, the fibers treated in accordance with the invention show a higher resistance to corrosion as well.

Claims

1. A process for removing of a matrix material from a bundle of metal fibers embedded in it, said matrix comprising a metal which differs from the metal of the fibers and whereby, the metal matrix is removed by an electrolytic process and in which the embedded bundle acts as an anode characterized in that the embedded bundle (1) is continuously transported through successive electrolytic baths (2, 4) containing an electrolyte at a temperature of at least 20 °C without making mechanical contact with current carrying contact elements and in which cathodic transition cells (6) are present between these baths and in which the current runs through the bundle (1) in transition zones (10) between these baths (2, 4) and cells (6) and in which at least part of the matrix material is deposited on cathodes (5) which are facing the bundle.
2. A process according to claim 1, in which the metal matrix consists of copper and the electrolyte contains H_2SO_4 and CuSO_4 .

3. A process according to claim 1, in which the metal matrix consists of copper surrounded by a steel jacket and in which the steel layer is removed in H_2SO_4 baths in a first series of cells (2) while the Cu is removed in $H_2SO_4/CuSO_4$ containing baths in a next series of cells (4).
- 5 4. A process according to claim 1, wherein the bundles are supported at the level or in the vicinity of the transition zones (10) where most of the current is conducted by the bundle (1).
5. A process according to claim 1, wherein the current supply for the electrolysis is regulated with a stabilized current and with current densities between 5 and 75 A/dm² of bundle surface.
- 10 6. A process according to claim 5 wherein the current is supplied by way of successive separated power supply circuits each of which serves one of the successive series of baths, and wherein a series of baths may contain one of more baths (2) resp. (4).
- 15 7. An apparatus for carrying out the process according to any of the claims 1 up to and including 6, characterized in that it contains successive electrolytic baths (2, 4) provided with cathodes (8, 5) and transition cells (6) present between the baths (2, 4) provided with anodes (7), means (11, 12) for the recirculation of the bath fluids to overflow sections (9) and power supplies (15) for the electrical current to the anodes and cathodes which are separated per series of baths and also wear resistant means (13) at the level or in the vicinity of the transition zones (10) for supporting the bundle being processed.
- 20 8. An apparatus according to claim 7, wherein the anodes (7) are made of lead.
9. An apparatus according to claim 7, wherein the cathodes (5) have a small adhesive affinity with respect to the deposited matrix material.
- 25 10. An apparatus according to claim 7, wherein all baths (2, 4) have lengths of not more than 75 cm.
11. Metal fibers obtained by the process of claim 1, characterized in that the average concentration of matrix metal in a surface layer of the fibers with a thickness of 5 nm is at most 0.2 % at.
- 30 12. Metal fibers according to claim 11, wherein they are stainless steel fibers with at least 10 % Cr by weight.
- 35 13. Stainless steel fibers according to claim 12, wherein they contain Ni and at least 16 % Cr.
14. Stainless steel fibers according to claim 13, wherein the average Cr/Cr + Fe + Ni ratio in their surface layers is between 1 % and 15 %, wherein the Cr, Ni and Fe contents are expressed in at %.
- 40 15. Fibers according to claim 14, wherein the average Cr/Cr + Fe + Ni ratio is less than 10 %.
16. Stainless steel fibers according to claims 14 or 15, wherein the average Cr/Ni ratio in the surface layers is less than 80 %.
- 45 17. Metal fibers according to claim 11, wherein they are refractory fibers containing Fe, Cr, Al, and optionally rare earths or Y.
18. Metal fibers according to claim 11, wherein their surfaces contain an average nitrogen content of at most 1.5 at %.
- 50 19. Stainless steel fibers obtained by the process of claim 1, characterized in that the average Cr/Cr + Fe + Ni ratio in the surface layers of the fibers is between 1 % and 15 %, wherein the Cr, Ni and Fe contents are expressed in at %.
- 55 20. Stainless steel fibers according to claim 19 wherein the average Cr/Cr + Fe + Ni ratio is less than 10 %.
21. Stainless steel fibers according to claims 19 or 20 wherein the average Cr/Ni ratio in the surface layers is less than 80 %.

Patentansprüche

1. Verfahren zum Entfernen eines Matrixmaterials aus ein m darin eingebetteten Metallfaserbündel, wobei die Matrix ein vom Metall der Fasern verschiedenes Metall aufweist und wobei die Metallmatrix durch einen elektrolytischen Prozeß entfernt wird, bei dem das eingebettete Bündel als eine Anode wirkt, dadurch gekennzeichnet, daß das eingebettete Bündel (1) kontinuierlich durch aufeinanderfolgende elektrolytische Bäder (2, 4), die einen Elektrolyt bei einer Temperatur von mindestens 20 °C enthalten, gefördert wird, ohne mechanischen Kontakt mit stromführenden Kontaktelementen zu machen, wobei kathodische Übergangszellen (6) zwischen diesen Bädern vorliegen, der Strom in Übergangszonen (10) zwischen diesen Bädern (2, 4) und Zellen (6) durch das Bündel (1) fließt und wenigstens ein Teil des Matrixmaterials auf Kathoden (5), die dem Bündel zugewandt sind, abgeschieden wird.
2. Verfahren nach Anspruch 1, bei dem die Metallmatrix aus Kupfer besteht und der Elektrolyt H_2SO_4 und $CuSO_4$ enthält.
3. Verfahren nach Anspruch 1, bei dem die Metallmatrix aus von einem Stahlmantel umgebenem Kupfer besteht und bei dem in einer ersten Gruppe von Zellen (2) die Stahlschicht in H_2SO_4 -Bädern entfernt wird, während in einer nächsten Gruppe von Zellen (4) das Cu in H_2SO_4 / $CuSO_4$ enthaltenen Bädern entfernt wird.
4. Verfahren nach Anspruch 1, bei dem die Bündel auf der Höhe oder in der Nähe der Übergangszonen (10) abgestützt werden, wo der meiste Strom vom Bündel (1) geführt wird.
5. Verfahren nach Anspruch 1, bei dem die Stromzufuhr für die Elektrolyse mit einem stabilisierten Strom und mit Stromdichten zwischen 5 und 75 A/dm² Bündeloberfläche reguliert wird.
6. Verfahren nach Anspruch 5, bei dem der Strom mittels aufeinanderfolgender getrennter Stromzufuhre Kreise zugeführt wird, deren jeder eine der aufeinanderfolgenden Bädersgruppen bedient, und bei dem eine Bädersgruppe eine oder mehr Bäder (2) bzw. (4) enthalten kann.
7. Vorrichtung zur Durchführung des Verfahrens nach irgendeinem der Ansprüche 1 bis zu und einschließlich 6, dadurch gekennzeichnet, daß sie aufeinanderfolgende elektrolytische Bäder (2, 4), die mit Kathoden (8, 5) versehen sind, und zwischen den Bädern (2, 4) befindliche Übergangszellen (6), die mit Anoden (7) versehen sind, Mittel (11, 12) für den Umlauf der Badfluide zu Überlaufabschnitten (9) und Stromquellen (15) für den elektrischen Strom zu den Anoden und Kathoden, die je Gruppen von Bädern getrennt sind, sowie abriebfeste Mittel (13) auf der Höhe oder in der Nähe der Übergangszonen (10) zum Abstützen des verarbeiteten Bündels aufweist.
8. Vorrichtung nach Anspruch 7, wobei die Anoden (7) aus Blei bestehen.
9. Vorrichtung nach Anspruch 7, wobei die Kathoden (5) eine geringe Haftaffinität gegenüber dem abgeschiedenen Matrixmaterial haben.
10. Vorrichtung nach Anspruch 7, wobei alle Bäder (2, 4) Längen von nicht mehr als 75 cm haben.
11. Durch das Verfahren nach Anspruch 1 erhaltene Metallfasern, dadurch gekennzeichnet, daß die Durchschnittskonzentration an Matrixmetall in einer Oberflächenschicht der Fasern mit einer Dicke von 5 nm höchstens 0,2 At.% ist.
12. Metallfasern nach Anspruch 11, welche nichtrostende Stahlfasern mit wenigstens 10 Gew.% Cr sind.
13. Nichtrostende Stahlfasern nach Anspruch 12, die Ni und wenigstens 16 % Cr enthalten.
14. Nichtrostende Stahlfasern nach Anspruch 13, wobei das Durchschnitts-Cr/Cr + Fe + Ni-Verhältnis in ihren Oberflächenschichten zwischen 1 % und 15 % ist und dabei die Cr-, Ni- und Fe-Gehalte in At.% ausgedrückt sind.
15. Fasern nach Anspruch 14, wobei das Durchschnitts-Cr/Cr + Fe + Ni-Verhältnis unter 10 % ist.

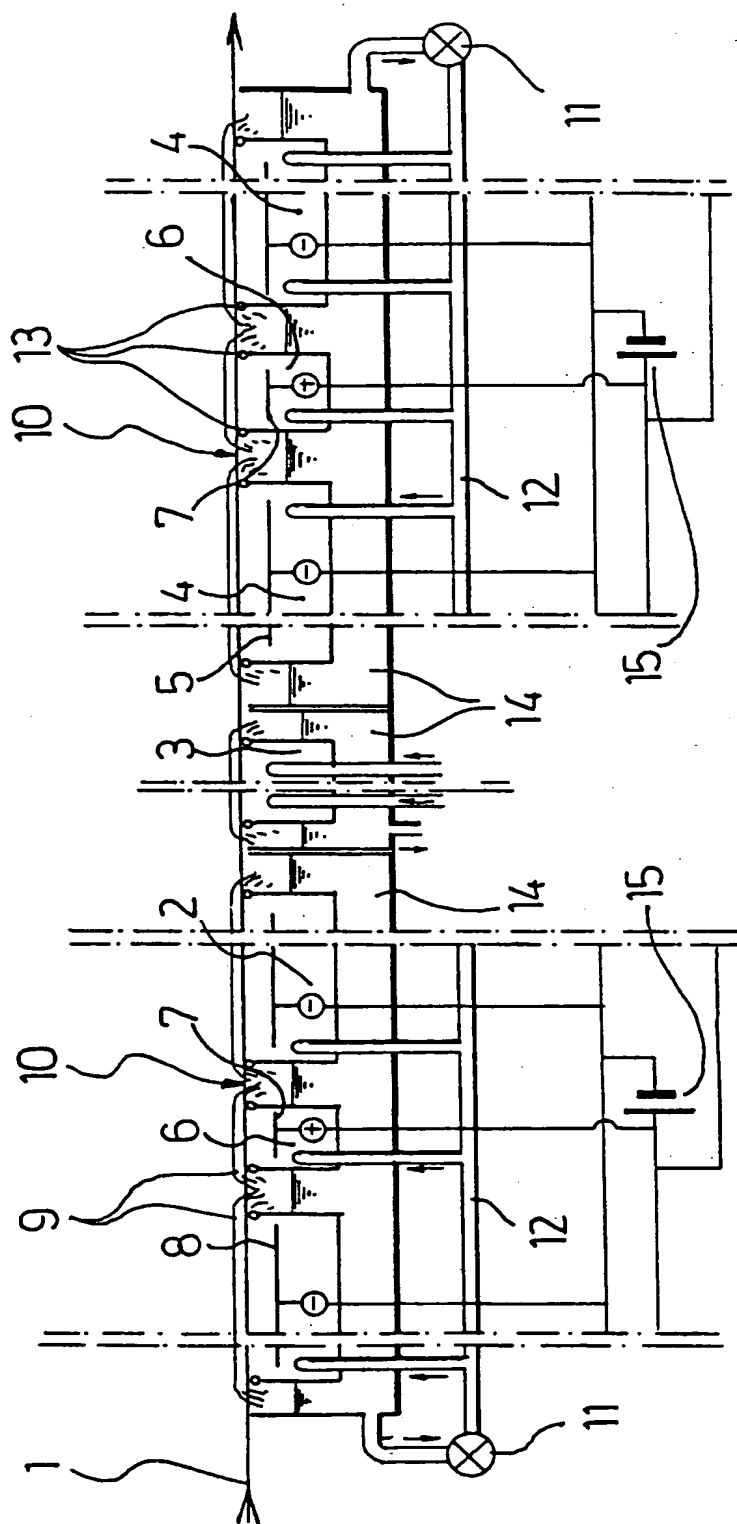
16. Nichtrostende Stahlfasern nach Ansprüchen 14 oder 15, wobei das Durchschnitts-Cr/Ni-Verhältnis in den Oberflächenschichten unter 80 % ist.
- 5 17. Metallfasern nach Anspruch 11, welche feuerfeste Fasern sind, die Fe, Cr, Al und fakultativ Seltene Erden oder Y enthalten.
18. Metallfasern nach Anspruch 11, wobei ihre Oberflächen einen Durchschnittsstickstoffgehalt von höchstens 1,5 At.% enthalten.
- 10 19. Durch das Verfahren nach Anspruch 1 erhaltene nichtrostende Stahlfasern, dadurch gekennzeichnet, daß das Durchschnitts-Cr/Cr + Fe + Ni-Verhältnis in den Oberflächenschichten der Fasern zwischen 1 % und 15 % ist, wobei die Cr-, Ni- und Fe-Gehalte in At.% ausgedrückt sind.
- 15 20. Nichtrostende Stahlfasern nach Anspruch 19, wobei das Durchschnitts-Cr/Cr + Fe + Ni-Verhältnis unter 10 % ist.
21. Nichtrostende Stahlfasern nach Ansprüchen 19 oder 20, wobei das Durchschnitts-Cr/Ni-Verhältnis in den Oberflächenschichten unter 80 % ist.

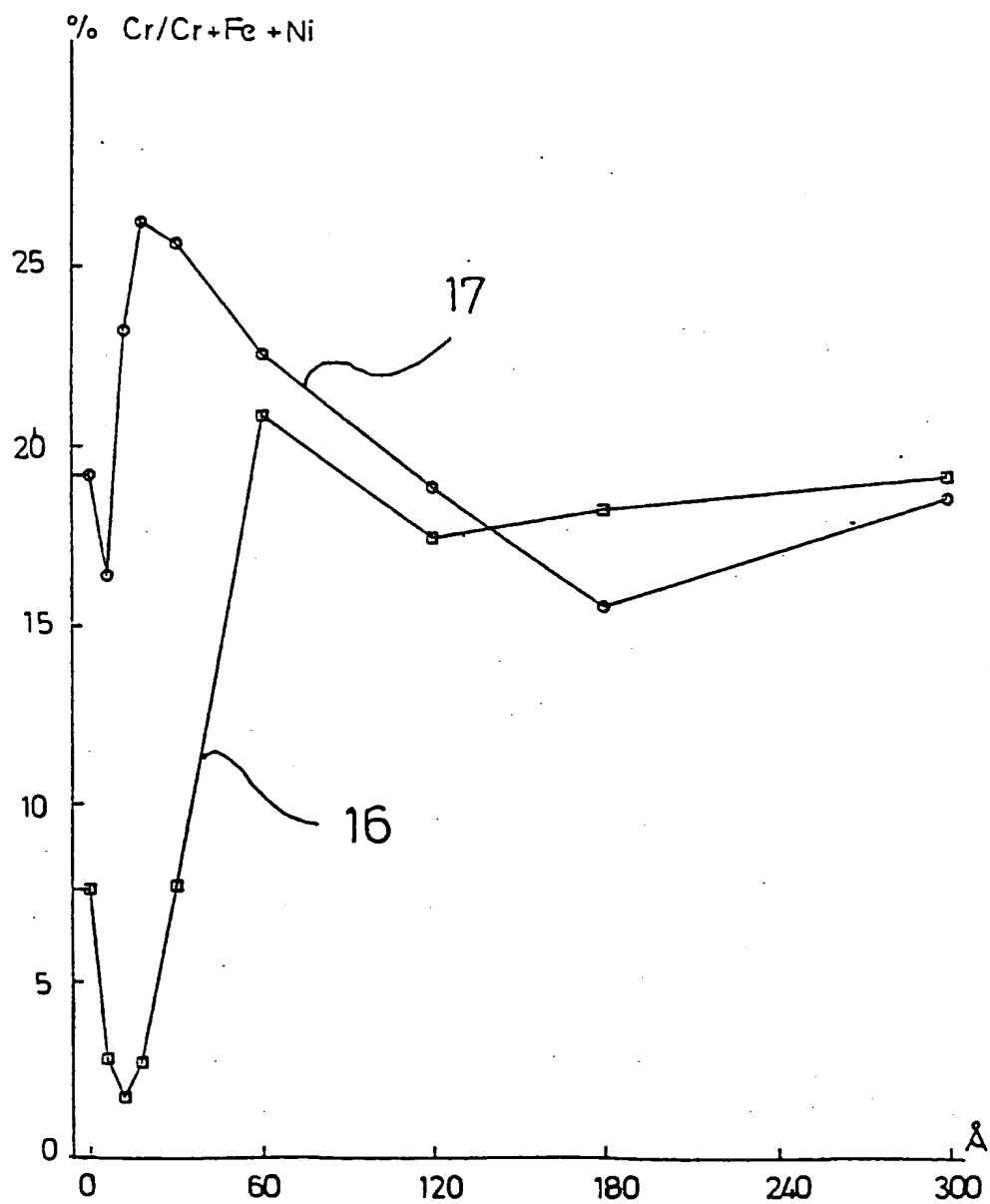
20 Revendications

1. Procédé d'enlèvement d'un matériau de matrice d'un faisceau de fibres métalliques noyé dans ce dernier, ladite matrice comprenant un métal qui diffère du métal des fibres, dans lequel la matrice de métal est retirée par un procédé électrolytique et dans lequel le faisceau noyé joue le rôle d'anode, 25 caractérisé en ce que le faisceau noyé (1) est transporté continuellement dans des bains électrolytiques successifs (2, 4) contenant un électrolyte à une température d'au moins 20 °C, sans entrer en contact mécanique avec des éléments de contact conducteurs, que des cuves de transition cathodiques sont présentes entre ces bains, que le courant passe par le faisceau (1) dans des zones de transition (10) entre ces bains (2, 4) et cuves (6) et qu'au moins une partie du matériau de la matrice est déposée sur 30 des cathodes (5) qui font face au faisceau.
2. Procédé selon la revendication 1, dans lequel la matrice métallique est en cuivre et l'électrolyte contient H₂SO₄ et CuSO₄.
- 35 3. Procédé selon la revendication 1, dans lequel la matrice métallique est en cuivre entouré d'une chemise d'acier et dans lequel la couche d'acier est retirée dans des bains de H₂SO₄ dans une première série de cuves (2) alors que le cuivre est retiré dans des bains contenant H₂SO₄ / CuSO₄ dans une série suivante de cuves (4).
- 40 4. Procédé selon la revendication 1, dans lequel les faisceaux sont portés au niveau ou à proximité des zones de transition (10) où la majorité du courant est conduite par le faisceau (1).
5. Procédé selon la revendication 1, dans lequel l'alimentation en courant pour l'électrolyse est régulée par un courant stabilisé et par des densités de courant comprises entre 5 et 75 A/dm² de surface de 45 faisceau.
6. Procédé selon la revendication 5, dans lequel le courant est fourni par des circuits successifs distincts d'alimentation en courant, dont chacun sert à une des séries successives de bains, et dans lequel une série de bains peut contenir un ou plusieurs bains (2) ou (4).
- 50 7. Appareil de mise en oeuvre du procédé selon l'une quelconque des revendications 1 à 6 compris, caractérisé en ce qu'il contient des bains électrolytiques successifs (2, 4) dotés de cathodes (8, 5) et des cuves de transition (6) présentes entre les bains (2, 4), dotées d'anodes (7), des moyens (11, 12) de recirculation des liquides des bains à des sections de trop-plein (9) et des alimentations en courant 55 (15) pour fournir le courant électrique aux anodes et aux cathodes qui sont séparées par des séries de bains ainsi que des moyens résistant à l'usure (13) au niveau ou à proximité des zones de transition (10) pour porter le faisceau en cours de traitement.

8. Appareil selon la revendication 7, dans lequel les anodes (7) sont en plomb.
9. Appareil selon la revendication 7, dans lequel les cathodes (5) ont une faible tendance à adhérer au matériau de matrice déposé.
- 5 10. Appareil selon la revendication 7, dans lequel tous les bains (2, 4) ont des longueurs inférieures ou égales à 75 cm.
- 10 11. Fibres métalliques obtenues par le procédé selon la revendication 1, caractérisées en ce que la concentration moyenne de métal de matrice dans la couche superficielle des fibres ayant une épaisseur de 5 nm est au maximum de 0,2 % en masse atomique.
12. Fibres métalliques selon la revendication 11, les fibres étant des fibres en acier inoxydable ayant au moins 10 % en poids de Cr.
- 15 13. Fibres en acier inoxydable selon la revendication 12, qui contiennent Ni et au moins 16 % de Cr.
14. Fibres en acier inoxydable selon la revendication 13, dans lesquelles le rapport moyen $Cr/Cr + Fe + Ni$ dans les couches superficielles est compris entre 1 % et 15 %, les teneurs en Cr, Ni et Fe étant exprimées en pourcentage en masse atomique.
- 20 15. Fibres selon la revendication 14, dans lesquelles le rapport moyen $Cr/Cr + Fe + Ni$ est inférieur à 10 %.
16. Fibres en acier inoxydable selon les revendications 14 ou 15, dans lesquelles le rapport moyen Cr/Ni dans les couches superficielles est inférieur à 80 %.
- 25 17. Fibres métalliques selon la revendication 11, les fibres étant des fibres réfractaires contenant Fe, Cr, Al et facultativement des métaux des terres rares ou Y.
- 30 18. Fibres métalliques selon la revendication 11, dont les surfaces présentent une teneur moyenne en azote d'au maximum 1,5 % en masse atomique.
19. Fibres en acier inoxydable obtenues par le procédé selon la revendication 1, caractérisées en ce que le rapport moyen $Cr/Cr + Fe + Ni$ dans les couches superficielles des fibres est compris entre 1 % et 15 %, les teneurs en Cr, Ni et Fe étant exprimées en pourcentage en masse atomique.
- 35 20. Fibres en acier inoxydable selon la revendication 19, dans lesquelles le rapport moyen $Cr/Cr + Fe + Ni$ est inférieur à 10 %.
- 40 21. Fibres en acier inoxydable selon les revendications 19 et 20, dans lesquelles le rapport moyen Cr/Ni dans les couches superficielles est inférieur à 80 %.
- 45
- 50
- 55

FIG.1



FIG.2

